

Review

Fire investigation and ignitable liquid residue analysis—A review: 2001–2007

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Abstract

Next to natural disasters fires cause some of the greatest losses to property and human life around the world. Arson, the deliberate setting of a fire to destroy property or to take a human life, is one of the most difficult crimes to investigate because much of the evidence at the scene is destroyed by the fire. Fortunately, the science of fire investigation is not static and more information to help investigators determine the origin and cause of a fire through careful examination of the scene and laboratory analysis of fire debris is published every year. This review article provides an overview of the scientific literature describing research and best practices in the fields of fire scene investigation as well as ignitable liquid residue analysis. This review is a compilation of articles published between late 2001 and early 2007. Conference proceedings for which full papers have not been published were intentionally excluded from this review. Some of the information contained in this review was presented at the 14th Interpol Forensic Science Symposium held in Lyon, France in October 2004.

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Keywords: Fire scene investigation; Fire dynamics; Ignitable liquid; Fire debris

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1. Scene examination and general fire investigation

1.1. *New books for the fire scene investigator*

Several new texts have been published with the intent of assisting the fire investigator. A new reference book, simply titled *Ignition Handbook*, provides extensive data about fire including a discussion on combustion theory as well as information on specific materials and devices from “accelerants in incendiary fires” to “wool” [1]. A new textbook, *Forensic Fire Scene Reconstruction*, applies forensic engineering techniques to fire scene reconstruction [2]. Another new book, *Fire Investigation*, is aimed at providing the fire scene investigator with the knowledge necessary to correctly determine whether a fire was accidental or malicious has also been published [3]. *Scientific Protocols for Fire Investigation*, is a well-written book for the fire scene investigator. This book gives many practical examples of lessons learned from the author’s own fire scene investigations and includes a chapter on the analysis of ignitable liquid residues [4]. The book *Investigation des Incendies de Véhicules Automobiles* was recently published in French [5] and is intended to assist scene investigators in the determination of the cause of vehicle fires (component/mechanical malfunction or incendiary), and to help identify common situations that result in vehicle fires. Two new books have been published that deal with the field of psychology and the profiling of criminal behaviour. The first book gives examples of different types of fire setters (e.g. experimental/curiosity, delinquent, thought-disordered, revenge, thrill seeker, and disordered coping) and some of the psychological theories behind why individuals turn to arson [6]. The focus of the second book is on behaviour profiling for different types of serial crimes, and has a single chapter devoted to the serial arsonist, including several short case studies [7]. While technically not a book, 37 full text articles from several conferences were compiled and made available electronically on compact disk in 2003 [8]. This compilation was been re-released in 2007 with a total of 83 articles [9]. Selected articles from these compilations have been cited throughout this review.

1.2. *General fire scene investigation*

General fire investigation was the topic of a number of articles. In a four part series, DeHaan explored the changes over the last 30 years that have occurred in the composition of furniture and floor coverings, the creation of many new

petroleum solvents and other related products, as well as improvements in analytical instrumentation, methods and sensitivity [10–12]. A shorter, revised version of part three in the series was published elsewhere [13]. A survey of the combustible contents in residential living rooms (lounges) has been compiled [14]. Guidance on the excavation of debris at a fire scene, and the information that can be gained from this process, has been provided [15], while the practical application of digital images in the reconstruction of a fire event has been described [16]. The need for scientific fire scene investigations has been expressed [17]. In a well-documented report two separate investigations were conducted into the “evidence” given by fire investigators that lead to the conviction of two men in the USA, one of whom was executed for the alleged crime [18]. This report highlighted the misinterpretation of “indicators” that the fire investigators believed to constitute evidence of arson, indicators that have been scientifically proven to be invalid [18]. Investigations of marine fires and explosions have been described [19]. A chance meeting between two fire investigation unit commanders led to the identification of a serial arsonist [20].

A selection of diverse fire scene investigations, including an accidental residential fire, a vehicle fire, and a suspected arson have been reported [21]. A case report has highlighted the importance of conducting a proper investigation into the origin and cause of a structure fire [22]. The causes of residential steam boiler failures and how these lead to fires have been explained [23]. Results from 48 tests showed that the ignition of flammable liquid vapours in the home by gas fired water heaters could be reduced by the elevation of the ignition source [24]. The conditions under which welding hoses may burst and result in a rapid flashback and fire/explosion have been described [25]. An unusual case where bricks soaked in kerosene were used in an attempt to initiate a fire at a polyethylene recycling plant was reported [26]. Match heads recovered from arson scenes were distinguished by inductively coupled plasma-atomic emission spectrometry [27]. An overview of boiling liquid, expanding vapour explosions (BLEVEs) has been published [28].

The preservation of a fire scene in which a fatality has occurred, and the securing of evidence, has been discussed [29]. A case study described the complexity of events that may be encountered when arson is combined with another incident such as suicide or murder [30]. An analysis of 75 Canadian homicides revealed that setting fire to the scene or to the victim’s body occurred in 3% of cases studied [31]. The effect

of arson on entomological evidence for the determination of the time elapsed since death was studied using pig carcasses in full scale burns [32]. The characteristics of burn injuries to the skin resulting from mineral–oil fires were reported [33]. A case describing a suicide by fire (self-immolation) was reported [34]. A retrospective look at suicides by fire in India, occurring between 1993 and 2003, indicated that kerosene was used in all cases and that the majority of people committing this act were young women [35]. The use of data mining techniques to improve intelligence analysis by exploring large crime databases has been reported [36]. Obtaining cellular telephone tower use data to determine the location of a suspect at the time a crime was committed was discussed [37]. A description of fire investigation in the context of a criminal investigation in Canada has been given [38]. A general discussion on the presentation of fire investigation evidence in a court of law was reported [39].

Improvements in fire investigation training over the last few decades in the UK have been discussed [40]. The need for fire scene investigators to acquire a broader understanding of criminal law and forensic science is described [41]. The hazards associated with the inhalation of toxic combustion gases, dusts, and other harmful vapours at a fire scene have been explored [42].

1.3. *Bush and wildland fires*

The literature on bush fire arsons have been extensively reviewed by the Australian Institute of Criminology [43]. The fact that more bushfires in Australia are deliberately set than those caused by lightning or other natural causes has led to the classification of deliberately lit bushfires by motive to improve investigator's understanding of why people light bush fires [44]. The potential for all terrain vehicles (ATVs) to ignite wildland fires was explored [45]. A study of wildland fires in north-eastern Florida showed that arson and lightning were the leading causes of fire and tended to be geographically clustered together [46]. Wildland arson incidents that occurred in five locations in Florida between 1994 and 2001 were modeled and shown to support an economic model of crime [47]. A forest fire arson scene in Italy, in which a woman died, was reconstructed to demonstrate the use of multiple delay-ignition devices combined with an ignitable liquid [48]. The use of large-scale forest fires as an act of terrorism has been discussed [49].

1.4. *Flashover and backdraft studies*

The phenomena of flashover and backdraft, and the differences between the two, have been discussed [50]. Some misconceptions around the flashover phenomenon were addressed in a series of letters [51]. A simplified mathematical model to investigate the physical, catastrophic mechanism of the backdraft phenomenon has been reported [52]. One study used a small compartment fire to demonstrate that a critical value of unburned fuel must be reached before backdraft can occur [53]. Backdraft in a tunnel occurs differently from that in a compartment fire and so experiments to simulate backdraft in

an underground mine tunnel were conducted [54]. The effects of flashover on common plastics have been studied using full-scale burn tests [55,56].

1.5. *Combustion studies*

While many articles on combustion and the combustion properties of materials are published every year, only those that were felt to be relevant to the fire scene investigator are discussed here. The physical properties of ignitable liquids were the subject of a few articles. The autoignition temperature of *n*-decane decreased with an increase in the initial pressure has been reported [57]. Different flammable limit test methods have been discussed and several observations with respect to standardization of these tests have been made [58]. An inter-laboratory study was conducted to determine the reliability of flash point measurements on ignitable liquids using either a manual or automatic testing apparatus [59]; the authors concluded that flash point data collected by either apparatus were equivalent. Another article discussed the estimation of flash points for both pure compounds and multi-component mixtures (e.g. solvents) [60]. Correlations between the closed-cup flash point of several organic compounds and the time to ignition, the time to peak heat release rate, and the propensity to flashover have been reported [61].

The results of full-scale test burns have also been published. The results of six test burns, both with and without the use of an ignitable liquid accelerant, that were conducted in a full scale, six storey wood frame building have been reported [62]. A study of fire-induced failure of polycarbonate windows in passenger railcars was published and demonstrated that larger railcar windows can fail up to twice as fast as smaller windows allowing more air to support the fire [63]. Full-scale room burns were used to determine a fire's origin by measuring the calcination depth in fire-exposed gypsum wall board [64]. The interpretation of the char pattern of wood from fire scenes has been discussed [65]. The thermal decomposition mechanisms and combustion reactions of polyurethane foam commonly used in furniture cushions have been studied and reviewed [66]. A study of the smouldering ignition of fire retarded polyurethane foam was conducted [67]. Temperature and heat flux measurements were performed in the flame and plume regions above cigarette lighters in order to test their propensity to ignite objects other than cigarettes [68].

Test burns conducted on pig carcasses demonstrated the ability of a localized fire to cause extensive destruction of a body [69]. Key elements identified in the study were the presence of adequate body fat together with a blanket wrapped around the carcass and the presence of carpet to act as a wick that would act together to establish a steady-state fire after initial acceleration of the fire by gasoline. The effect of cloth to act as a wick in the combustion of tissue from a human leg and the susceptibility of bones of differing densities to incineration was also reported [70].

The ignition of a single drop of either automotive or aviation fluids on a hot, horizontal flat plate have been tested [71]. Another study reported that gasoline would only autoignite on a

hot manifold if the manifold temperature exceeded 750 °C, a temperature well above the reported autoignition temperature of 257–280 °C for automotive gasoline [72].

Test burns to simulate the intentional ignition of plastic domestic heating oil tanks have been reported [73]. The reconstruction of events leading up to a liquefied petroleum gas (LPG) explosion and fire at a petrochemical processing plant in India, the resulting damage, and dispersion modeling of the vapour cloud that caused the incident, have been reported [74].

1.6. Modeling and fire dynamics simulation

The latest software versions of the Fire Dynamics Simulator (FDS) and Smokeview, programs used to model fire behaviour, were released by the National Institute for Standards and Technology (NIST) [75]. The Fire Dynamics Simulator is a computational fluid dynamics model of fire-driven fluid flow which solves numerically a form of the Navier–Stokes equations appropriate for low-speed, thermally driven flow with an emphasis on smoke and heat transport from fires. Smokeview is a visualization program that is used to display the results of an FDS simulation. This software is available at no cost from the NIST web-site (www.fire.nist.gov). An overview of the two main fire models used in fire investigations (zone models and field models), and how these may be used to evaluate fire origin and cause hypotheses, has been presented [76]. Various kinds of fire tests and computational models, and the limitations and abilities of each have been described in part one of a two part series [77]. The second part in the series illustrated the concepts described in part one using 10 case studies from real investigations [78]. An overview of the current state of fire research, and in particular, fire modeling, has been reported [79].

The zone model FIREWIND was used to simulate different fire scenarios for retail shops [80]. The Fire Dynamics Simulator software was used to investigate smoke movement in a large building space, including the use of different smoke exhaust systems [81]. Three accidental fires in single-family residences have been modeled [82]. The results of experiments designed to model fire behaviour have been also been reported. A full-scale test burn to simulate the burning of pressurized hydraulic fluid in a large industrial facility was presented [83]. The test burn was designed to simulate a fire at a food processing plant where 25 people died and the full-scale test results were compared to computer model results generated by NIST FASTlite software [83]. Ignition tests and scale model burn tests were used to model the behaviour of a discotheque fire in which 63 people died [84]. A nightclub fire was used to illustrate various rates of fire growth and smoke evolution based on a fire model [85]. The reconstruction of an arson in a Swedish psychiatric hospital concluded that the PVC flooring used in the building led to tragic results [86].

A mathematical model was developed from experiments of both spontaneous and piloted ignition of wood and was used to predict the time to ignition of wood under different conditions [87]. The ignition time of wood when exposed to an external heat source was also modeled and the authors found good

agreement between their theoretical model and experimental data [88]. Experiments on two different species of wood were carried out in order to study the ignition process of wood when exposed to a variable heat flux [89]. The effect of heating on a long span truss floor system has been simulated [90].

The effect of longitudinal ventilation systems on the development and spread of fire within a road tunnel in which a fuel spill has occurred were studied [91–93]. The size of a pool fire and ventilation velocity were identified as key factors that will affect the development and spread of a fire and that there is a more pronounced effect for a fire involving a heavy goods vehicle than for a car [91,92]. Large truck and trailer fires (heavy goods vehicles) in a road tunnel were conducted to collect gas temperature data at the tunnel ceiling [94] as well as calculate the heat release rate from mixed commodity loads [95].

Computational fluid dynamics software was employed to predict the airflow behaviour and, therefore, the fire and smoke spread in a McDonnell Douglas MD-11 commercial aircraft [96]. The modeling of fire behaviour in the upward spread of flame on a flat vertical surface was reported [97]. Theoretical formulas for fire growth under external radiant heating have been reported [98]. A radiation heat-transfer-based model was used to determine that the separation distances governed by US regulations are adequate for liquefied petroleum gas storage tanks exposed to radiant heating [99].

The characteristics of a candle flame were both measured experimentally and modeled by computer [100]. The burning behaviour of candles under controlled laboratory conditions and using a fire dynamics simulator was investigated [101].

A heat and mass transfer theory for liquid fuel burning on carpet, validated by small-scale test burns, has been described [102]. The potential explosion hazard resulting from flammable vapours generated from a spill of liquid fuel in a variety of indoor environments was modeled [103]. Using full-scale spill and fire experiments, one study attempted to predict the quantity of liquid fuel (gasoline or kerosene) required to create burn patterns of a specific size on vinyl, wood parquet, and carpet covered plywood floors [104]. Guidelines for the calculation of how fast a pool of spilled liquid will spread across a surface, evaporate, and potentially form a flammable mixture with the air have been published [105].

1.7. Electrical fires

How electrical wiring faults can lead to over-heating and result in a structure fire has been described [106,107]. A hazardous electrical connector used to join electrical wires together in a light fixture has been reported [108]. Significant heating at the plug (up to 200 °C) was reported in a study of a loose connection between plug and receptacle combined with an overcurrent [109]. The authors found that the heat generated degraded the polyvinyl chloride (PVC) plug insulating material which decreased the arc tracking resistance of the plug (i.e. arcs through char), eventually resulting in fire. Rubber and PVC insulated electric cords were tested for physical shorts (i.e. metal-to-metal contact) and arc tracking under radiant heat and

a variety of conditions, including twisting and pinching of the cord [110]. The inhibition of heat transfer from household electrical wiring when it is surrounded by polyurethane “spray-in” foam insulation and the resulting lack of heat transfer from a loaded circuit may raise the temperature of the wire to the point of ignition [111]. The risks associated with the use of non-laboratory grade microwave ovens to perform chemical reactions in the presence of a flammable solvent have been described [112]. Some criteria to assist the fire investigator in determining the cause of an electrical fire have been reported [113].

The non-destructive examination of materials from electrical fires has been described in the literature [114,115]. Raman spectroscopy and SEM-EDX were used to distinguish between primary and secondary molten (arc) marks by examination of the carbon residue remaining on molten marks caused by the short-circuit of PVC-coated wire [116]. Arc beads have also been analyzed using secondary ion mass spectrometry (SIMS) to determine whether a primary or secondary short-circuit had occurred [117]. A detailed review of the methods used to distinguish primary (“cause”) and secondary (“victim”) arc marks have been presented [118,119]. X-ray analysis was used to analyze a bead of tin-lead solder from a wire recovered from a large fire [120]. Laboratory tests were conducted to understand the behaviour of switchboard arcs and the information used to analyze real switchboard arcing events to help determine the cause [121].

A gasoline re-fueling fire at a commercial filling station has been used to illustrate what conditions can lead to a fire caused by static discharge [122].

1.8. Vehicle fires

The results of test burns on motor vehicles have been reported [123]. Full-scale test burns on passenger vehicles as well as test burns on a large number of car materials and commercial plastics have been conducted [124]. The fire behaviour of passenger cars, electronic cabinets, and electric ignition sources were studied experimentally and by the use of computer models [125]. A reconstruction of a fatal fire that occurred in a parked motor vehicle was reported [126]. The results of an investigation into a vehicle fire that occurred in a cross-harbour tunnel in Hong Kong have been discussed [127]. An unusual case was reported in which a person committed suicide by fire while enclosed in the trunk of her vehicle [128]. Two cases of suspected fraud involving fire damage to motor vehicles have also been reported [129,130].

1.9. Spontaneous ignition

The vast majority scientific publications on spontaneous ignition come from the coal industry and were not considered to be relevant to the typical fire scene investigator; however, there are a few studies describing the self-heating of other materials that have been reported in the literature. For example, the spontaneous heating of oils [131], as well as rubber tires and rubber mats [132] have been reported. The spontaneous ignition

of different types of plant material, including Eucalyptus leaves and sawdust, that have occurred at composting and mulching operations has been described [133]. The spontaneous ignition of refuse derived fuel and meat bone meal caused by wetting and fermentation at room temperature has been reported [134]. A study of spontaneous heating of shale deposits that were excavated and piled during the preparation of a sanitary landfill was reported [135]. A study of cotton bales demonstrated that they do not pose a fire hazard provided the bales are compressed to a minimum density of 360 kg/m³ [136]. It has been shown that bags containing up to nine kilograms of charcoal briquettes cannot self-ignite at ambient temperature [137]. The technical aspects of spontaneous combustion of laundry in tumble dryers using “thermal ignition” theory [138] and “hot spot” theory have been reported [139].

The existence of “pyrophoric carbon” and its implications to a fire investigation has been debated in the literature over the years. In the continuing debate of the existence of pyrophoric carbon Babrauskas has written a commentary in support of chemical changes, not just physical changes, in the wood structure as the cause of self-heating of wood [140]. A rebuttal was subsequently published by Cuzzillo et al. [141] to which Babrauskas replied [142]. While Babrauskas suggested that additional experiments be conducted [140,142], and Cuzzillo et al. have welcomed this idea [141], the debate continues with no new scientific information being proffered at this time.

1.10. Accelerant detection canines

A small body of work has been reported in the literature regarding the training and handling of accelerant detection canines. The effects of training canines sequentially on different odours were explored [143]. It was found that the canine’s ability to recognize previously learned odours did not decrease as the number of substances trained increased, and that the amount of time required to train a canine on a new odour decreased as more odour discriminations were learned [143]. A device designed to allow a canine’s sniffing behaviour under a variety of situations to be studied, and to determine whether or not a canine was actually sniffing during a search, was described [144]. Another study found that strenuous physical activity increased the rate of panting and led to a significant decrease in the canine’s ability to detect explosives [145]. While not directly related to arson, another study showed that odour concentration is used by canines to pin-point their target [146].

An article that looks at the training and use of accelerant detection canines at fire scenes, and the costs involved in maintaining a dog/handler team, has been published [147]. The need to create a national standard for canine teams has been discussed [148]. A best practice guide for the proper care and deployment of accelerant detection canine teams was released by the Office of the Deputy Prime Minister, United Kingdom (UK) [149]. The Scientific Working Group on Dogs and Orthogonal Detection (SWGDOG) has provided some guidelines on the certification and maintenance of certification for detection canine teams [150]. The relationship between handler

and dog, both at work and home, has been described for police dogs, and accelerant detection canines [151].

1.11. Field portable devices

Very little work has been published in the last 7 years on the use of field portable electronic devices to assist the fire investigator at the scene. One article evaluated the ability of field portable electronic noses to their ability to detect ignitable liquids at a fire scene [152]. Another study investigated the use of a portable gas chromatograph for the detection of ignitable liquids in fire debris and found the instrument tested to be unsuitable for the task [153].

1.12. Evidence collection and preservation

A study found that exhaust from vehicles or power equipment operated near a fire scene would be insufficient to contaminate samples taken from the scene [154]. Footwear worn by individuals at a fire scene will not “track” ignitable liquid residues from one location to another within the scene [155]. Results from samples collected from full-scale room burns using an accelerant detection canine and a commercial ignitable liquid absorbent were compared to laboratory analysis by GC–MS [156]. The suitability of a variety of commercially available absorbents to collect ignitable liquid residues from concrete has been reviewed [157]. Some general guidance on fire scene security and the preservation of evidence has been presented [158]. A general discussion of the legal aspects, under Canadian law, of the preservation of evidence from a fire scene has been discussed [159].

1.13. Retrospective fire incident reviews and fire statistics

The publication of fire statistics and retrospective reviews of fire incidents can provide valuable information for fire investigators. A few publications described the incidence of fire and explosions in industry and the workplace, as well as an analysis of dwelling fires, in London, UK. One review examined incidents of fires, explosions, runaway chemical reactions and unignited releases of flammable materials at work sites in the UK between 1 April 1998 and 31 March 2000 [160]. This review reported 2220 incidents of workplace fire and explosions that resulted in 729 injuries and 19 deaths. Another review recounted 3819 fires in the work place that occurred between 1996 and 1999 [161]. This review included analysis of “residential workplace” fires (e.g. hotels, boarding houses and hospitals), as well as office and commercial fires, and identified which type of workplace was more likely to suffer from a deliberate or accidental fire. Another article identified common risk factors based on an analysis of 259 fatal, unintentional dwelling fires that occurred between 1996 and 2000 in London, UK [162]. Although not the focus of the article, the authors noted that 61 (17%) deaths resulted from deliberately set fires. An analysis of fire incidents in London, UK was undertaken to determine the types of situations that lead to large losses, rapid growth rates, and extended time delays [163].

The United States of America (USA) is the source of a number of statistical reports on fire and arson. A statistical summary of the fire losses in the USA during 2001 documented 521,500 structure fires, approximately 45,000 of which were incendiary in nature [164]. This summary reported that intentionally set structure fires resulted in 330 civilian deaths and \$1 billion in property losses (not including the deaths and property damage from the World Trade Centre attack on 11 September 2001). Similar reports have been published describing the fire losses in the USA during 2002 and 2005 which showed small decreases in the number of structure fires and incendiary fires over the years [165,166]. An analysis of major fires in the USA indicated that 38% of large fires in 2002 were the result of arson [167].

A study of fires in the USA identified key characteristics of buildings and their occupants that would increase the risk of fire-related casualty [168]. A study of 194 unintentional injuries sustained by Americans involved in the burning of garbage or brush identified the use of an accelerant (e.g. gasoline) in over 80% of the injuries [169]. Fatal, unintentional injuries occurring in USA homes between 1992 and 1999 were assessed and found that fire/burn death rates were highest among children [170]. A total of 379 fatal fires that occurred in a USA county were examined and found that smoking materials were the leading cause of these fires [171].

Surveys of fires from other parts of the world were also published. For example, one report surveyed 243 fires and explosions that occurred at German companies involved in the woodworking industry [172]. Another review examined 69 suicides by fire in South Africa where it was found that an accelerant (typically kerosene) was used by the majority of the victims (53 or 77%) [173]. Statistics from over 60,000 fire incidents occurring between 1996 and 2004 in Jordan have been reported [174]. An evaluation of structure fires in Finland explored the correlation between the ignition frequency, building category, floor area, as well as date and time of the fire [175]. A similar study examined structure fires in Taiwan and concluded that industrial buildings had the highest annual fire ignition rate, followed by residential buildings [176].

A unique review of the incidence of operating room fires provided information on how these fires can be extinguished and even prevented [177].

1.14. The psychology of fire setters

While not directly related to fire scene investigation, there is a need for fire investigators to have at least a rudimentary understanding of the psychology of people who set fires. The psychological profiling of serial arsonists was studied extensively and four discrete behaviour patterns of serial arsonists, which may prove helpful to the fire investigator, were identified [178]. According to another report a serial arsonist does not necessarily suffer from pyromania, and fires resulting from true pyromania may not be as frequent as once assumed [179]. The relationship between the characteristics of an offender and the actions displayed at the arson scene has been discussed [180]. A case report was used to demonstrate the

most important issues in evaluating a person's fire setting behaviour [181]. The effect of employment volatility on the economic marginalization of an individual and the subsequent increase in criminal activity such as arson and property crime has been studied [182].

Offences committed by the schizophrenia sufferer, including arson, have been characterized [183]. A report concluded that schizophrenics commit mainly violent acts, and are especially prone to fire setting [184]. A case study of an arson committed by a person suffering from hyperglycemic delirium has been reported [185]. A review of arsons in Croatia from a psychiatric point of view has been reported [186]. A discussion on the risk factors as well as possible medical treatment for pathological fire setters has been published [187].

A study of pre-adolescent (age 4–9 years) fire setters, and the physical and social factors that led to their fire setting activity, has been reported [188]. The potential predictors of arson recidivism in children and adolescents have been discussed [189]. Assessments of the affect of physical and social environment on adolescent arson have been presented [190,191]. A survey of pre-dominantly young male arsonists examined their psychological motives and found that more than half of the offenders had been diagnosed with a psychiatric disorder [192]. A group of adolescent male fire setters were compared to a group of non-fire setting males in order to assess the factors involved in fire setting behaviour and what intervention programs may be of benefit in preventing such activity [193]. Statistical data have been published describing the characteristics of juvenile fire setters (age, gender and family unit) and included incident characteristics such as types of structures, month of occurrence, and ignition sources [194]. Indicators of juvenile fire setting, such as time of day and location, have been outlined [195].

The profile of convicted arsonists in the UK was shown to have shifted significantly between 1951 and 2001 with previous convictions for violent acts and reconviction for arson becoming more common in the later decades [196]. In a review of 26 cases involving multiple homicides (73 deaths in all), four deaths were reported to have been the direct result of fire [197]. A literature review of the recidivism rate of arsonists has been published [198]. A psychiatric review of arson recidivists showed that the majority (68%) were intoxicated by alcohol at the time the crime was committed [199]. A study of 45 serial arsonists in New Zealand revealed that approximately half started fires close to a home base, whilst the other half commuted to their targets [200]. A study on the successful profiling of serial arsonists showed that a successful profiler must be skilled at objective and logical analysis [201]. Data from 76 commercial robberies in Finland were analyzed to determine the accuracy of predicting the residential location of a serial offender [202]. While this study did not look specifically at data for serial arson, some conclusions were drawn from the study suggesting the appropriateness of using this technique to further develop tools for the identification of a serial arsonist's home [202]. An investigation into a serial fire setter has been reported [203].

2. Laboratory analysis of ignitable liquid residues

2.1. New books for the laboratory

A new book, *Analysis and Interpretation of Fire Scene Evidence*, is written for the chemist and is intended to bridge the disciplines of fire investigation and forensic arson analysis [204]. While the book *Scientific Protocols for Fire Investigation* was chiefly written for the fire scene investigator, this book does include a chapter on the analysis of ignitable liquid residues [4].

2.2. General ignitable liquid analysis

The role of the National Centre for Forensic Science (NCFS) in sponsoring the Technical Working Group for Fire and Explosions (TWGFEX) and fostering the development of national guides for the collection and analysis of fire and explosion debris has been described [205]. Two reviews, one describing the American Society for Testing and Materials (ASTM) standards for fire debris analysis [206], and the other listing recent advances in a variety of areas related to fire debris analysis, have also been published [207]. An overview of the first five collaborative tests for ignitable liquid analysis conducted by the Fire and Explosion Investigation Working Group of the European Network of Forensic Science Institutes (ENFSI) has been reported [208]. The analytical methods used in a fire investigation have been described [209]. The analytical techniques commonly employed in fire scene investigation and laboratory analysis have been reviewed [210].

2.3. Sampling and sample preparation techniques

A general review article describing the use of static and dynamic headspace extraction, solid phase micro-extraction (SPME), and other techniques that have been used in forensic science has been published [211]. A brief history of the development of SPME and a short literature review of SPME applications in forensic science, including ignitable liquid extractions, has been reported [212]. The ASTM has published new guidelines for the use of solid phase micro-extraction (SPME) as a preparative technique for fire debris analysis [213]. The desorption of SPME fibres using a small volume of solvent followed by conventional analysis using an autosampler connected to a gas chromatograph–mass spectrometer (GC–MS) was reported [214]. A study of the selectivity of polymethylsiloxane (PDMS) and Carboxen/PDMS SPME fibres for headspace sampling of fire debris samples found not only that aliphatic and aromatic compounds were preferentially extracted, but also that the compounds extracted varied depending on temperature and fibre type [215]. Field sampling of workplace air contaminants following a fire using SPME and GC–MS showed that the portability of the SPME sampling technique may be used in fire scene investigations [216]. SPME was used to analyze soot for the presence of polycyclic aromatic hydrocarbons in gasoline [217]. A report comparing the results from air samples collected at simulated fires using either a SPME fibre or a tube packed with Tenax and

CarbopackB showed that volatiles in the air were more effectively trapped with an adsorbent-packed sampling tube than with a SPME fibre [218]. A main drawback of SPME analysis is that the fibres cannot be re-used because they are easily broken. A new, more robust type of SPME fibre was constructed from titanium wire and coated using a sol-gel process [219]. The main disadvantages of SPME, lack of automation and fragility of the fibres, have been addressed in a review article [220].

Two adsorbents, Tenax TA[®] and Carbotrap 300[®], were evaluated for their usefulness as passive adsorbents of ignitable liquid residues [221]. A study reported on a number of solvents and solvent mixtures that could be used to desorb activated charcoal strips in place of carbon disulfide [222]. Distortions of the chromatographic profile from samples adsorbed onto activated charcoal have been described [223]. An experiment designed to demonstrate simplex optimization to university students reported that optimal enrichment conditions for extracting samples of gasoline, lighter fluid, paint thinner, kerosene, and diesel fuel onto activated charcoal strips can be achieved in less than 5 h [224]. Supercritical fluid extraction (SFE) was used to extract petroleum hydrocarbons from soil [225]. Optimized conditions for SFE of petroleum-based fuels from fire debris have been reported [226]. Even though steam distillation has been all but abandoned by the fire debris analysis community, a recent article has described the efficacy applying micro-steam distillation directly to fire debris [227].

The results of sampling the skin of human volunteers for the presence jet fuel has been reported [228]. Another report described the post-mortem exposure of the skin of rats to kerosene and the subsequent detection of kerosene on the skin after the skin was burned [229]. Volatiles from perfume sprayed onto human skin were collected using a flexible polydimethylsiloxane tape and the results compared with extractions using SPME fibres; this technique, known as sorptive tape extraction (STE), could have applications in the recovery of ignitable liquid residues from human skin or other surfaces such as concrete [230].

2.4. Chromatographic analysis

The field of gas chromatography (GC) is continually expanding. Emerging techniques such as gas chromatography–isotope ratio mass spectrometry (GC–IRMS) and multi-dimensional gas chromatography (two- and three-dimensional GC as well as GC \times MS) are currently being explored in other scientific fields such as geochemistry and environmental chemistry; however, their potential to be used in the forensic examination of fire debris and ignitable liquids is clear. Some examples of these, and other techniques, are provided in this section.

The use of GC–MS–MS to analyze fire debris samples for gasoline in the presence of other, potentially interfering pyrolysis products has been described [231,232]. GC–MS–MS was used to increase target compound selectivity and sensitivity which allowed the development of an “expert system” for pattern recognition of ignitable liquids in fire debris samples

[233]. A GC–MS–MS method for detecting alkylbenzenes, naphthalenes, and anthracenes in fire debris samples spiked with gasoline has been described [234].

Comprehensive, two-dimensional gas chromatography (GC \times GC) is a recent development that has received a lot of attention in the scientific literature over the past few years [235,236]. In GC \times GC the entire sample undergoes a two-dimensional separation with all of the components being separated first by boiling point and then by polarity. The sample is first separated conventionally on a non-polar column; the effluent from the first column is precisely modulated into sharp chemical pulses that then undergo a second, fast separation on a shorter, polar column. The effluent from the second column then goes to a detector. The resulting output consists of two orthogonal retention time axes, one for each column. The key element in GC \times GC is the modulator and much work has focused on this aspect of the technique [237]. A simplified cryogenic modulator was constructed and used to analyze *n*-C8 to *n*-C18 alkanes. A different modulator was developed and used to analyze a light petroleum condensate [238]. A new liquid nitrogen cryogenic modulator was developed for the analysis of very volatile compounds such as those found in gasoline [239]. A flow-switching technique was used in GC \times GC analysis of gasoline to effect a complete separation of the aromatic compounds [240]. The criteria necessary to optimize conditions for GC \times GC have been described [241]. The reproducibility of GC \times GC retention times, based on an intra-laboratory study, was reported [242]. Different ways of displaying and interpreting GC \times GC data of a gasoline have been presented, but the authors caution that the interpretation of two-dimensional chromatograms is a complex process that cannot be easily standardized [243]. Compound retention times in two-dimensional space have been predicted [244]. A method for the subtraction of background levels from GC \times GC chromatograms has been described [245]. The separation of petroleum products using GC \times GC has been described [246]. Examples of gasoline samples that have been analyzed by GC \times GC have been published [247]. The use of GC \times GC to characterize heavy petroleum distillates has been described [248]. A two-dimensional separation of diesel fuel using GC \times MS was compared with a GC \times GC separation technique [249]. Finally, GC \times GC was used to separate ignitable liquids from samples of fire debris [250].

The technique of GC–IRMS was initially developed to characterize crude oil and has been used in geological surveys of crude oil deposits and in the determination of the source of an oil spill. The environmental forensic applications of this technique to compare fuel samples are obvious and have resulted in this technique being recently applied to the characterization of gasoline samples [251,252]. A tandem GC–isotope ratio technique permitting the determination of both the carbon and hydrogen isotopic compositions of individual compounds in a complex mixture has been described [253]. The potential use of GC–IRMS in characterizing ignitable liquid residues in fire debris has been discussed [254]. A description of isotope ratio mass spectrometry (IRMS) and its applications to forensic science, including the

discrimination of ignitable liquids, has been reported [255]. Compound specific isotope analysis (CSIA) was applied to oil samples to determine the potential source of an oil spill [256].

Transition-phase chromatography, a technique where different mobile phase conditions exist inside the same column, has been applied to the separation of fuels [257].

2.5. Other analytical methods

Less commonly available analytical techniques have been applied to the analysis of ignitable liquids. A homebuilt Fourier-transform ion cyclotron resonance mass spectrometer (FT-ICR MS) was used to obtain high resolution mass spectral “fingerprints” of a variety of petroleum products [258]. An ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectrometer was used to characterize crude oil and its distillates [259]. Although membrane introduction mass spectrometry (MIMS) has not yet been directly applied to the field of fire analysis, it has received a lot of attention in the field of environmental analysis and is the subject of a review article [260]. It has been shown that MIMS can be used to monitor the benzene, toluene, ethylbenzene and xylenes (BTEX) concentrations in water after contact with gasoline [261].

The use of vapour phase ultra-violet (UV) spectroscopy for the analysis of fire debris samples has been described [262]. Fluorescence spectra generated by time-resolved spectroscopy with a pulsed Nd-YAG laser was used to identify various ignitable liquids on a variety of substrates, including newspaper, carpet, and wood [263]. Analysis of the polar compounds in some types of fuels was conducted, without prior chromatographic separation, using a flow injection analysis/electrospray ionization/mass spectrometry technique [264].

2.6. Analysis of liquids, new products and other materials

The analysis of the wax content of artificial fire place logs from different manufacturers by high temperature gas chromatography (HT-GC) has been reported [265]. Samples of liquid jet fuel were analyzed by GC and the results compared to the analysis of the same samples by headspace gas chromatography [266]. An in depth review article on the toxicological effects of turpentine contains a wealth of valuable information on the history, production and chemical composition of this natural product [267].

Biodiesel fuel, a fuel with physical characteristics similar to petroleum diesel fuel but is derived from oils of biological origin (e.g. soybean, rapeseed and sunflower), is well established in Western Europe and is an emerging market in the North American fuel industry. It has been reported that Germany, Austria and Sweden use 100% pure biodiesel (B100) in adapted vehicles [268]. In France, biodiesel is supplied as either a 5% (B5) or a 30% blend (B30) with petroleum diesel fuel [268], while in Italy a 5% blend (B5) is commonly used [268]. In some regions of the USA and Canada biodiesel is marketed as a 20% blend with petroleum diesel fuel (B20) [269]. It is anticipated that fire debris analysts will eventually

see biodiesel fuels in casework. A comparison of different chromatographic techniques, including high-pressure liquid chromatography–mass spectrometry (HPLC–MS), for the analysis of the acylglycerols and methyl esters of fatty acids in biodiesel has been reported [270]. A plethora of chromatographic and spectroscopic methods, such as gas chromatography, gel permeation chromatography, HPLC, MS, infrared spectroscopy (IR) and nuclear magnetic resonance spectroscopy (NMR), including their advantages and disadvantages, for the analysis of biodiesel fuels have been described [271]. A brief introduction to biodiesel and its analysis by gas chromatography has been described [272]. The methyl esters present in biodiesel have been characterized by gas chromatography [273]. A primer on biodiesel and its analysis has been presented from the perspective of a fire debris analyst [274].

The analysis of vegetable oils by gas chromatography–mass spectrometry (GC–MS) was reported [275]. The analysis of fire debris samples for the presence of vegetable oils has been described [276,277].

2.7. Data interpretation

The uncertainty of forensic fire origin and cause investigations, and the use of a Bayesian network to assist in the interpretation of finding residual ignitable liquid in fire debris, has been discussed [278]. A Bayesian network was applied to two cases, one in which terpenes were identified in the fire debris and the other in which gasoline was detected [279]. The use of alkylcyclohexane compounds to identify kerosene residues in the presence of pyrolysis products from various types of plastics has been reported [280]. The effect of type of material burned, type of accelerant applied, and length of burn time on the detection of ignitable liquid residues was examined [281]. The use of using UV spectroscopy, GC–MS, and pyrolysis-GC to analyze smoke and other residues of combustion for the presence of gasoline has been reported [282]. A variety of medium-range ignitable liquids showed that commercially available products have a broad range of compositions, some of which may be difficult to classify [283]. The effects of microbial action in soil on the chromatographic profile of automotive gasoline, a barbecue starter fluid (medium petroleum distillate) and a diesel fuel (heavy petroleum distillate) were reported [284]. The changes in hydrocarbon distribution patterns of diesel fuel spills resulting from long-term anaerobic microbial degradation have been reported [285].

2.8. Chemical fingerprinting

Interest in the discrimination between samples of liquid gasoline has experienced a recent resurgence. An approach to gasoline comparisons has been briefly described [286]. Gasoline samples ranging from no evaporation to 50% evaporation were differentiated by comparing the ratios of sequential peaks obtained from GC–MS analysis [287]. The discrimination of unevaporated gasoline samples by applying principal component analysis (PCA) to the C0- to C2-naphthalene profiles obtained

from GC–MS analysis was reported [288]. This initial work was expanded and the method used to discriminate gasoline samples that were up to 90% evaporated [289,290]. PCA applied to GC–MS data was combined with artificial neural networks (ANN) to classify unevaporated regular and premium gasoline samples [291]. A study of 16 gasoline samples (50% evaporated), extracted from fire debris using headspace analysis, showed that all samples could be distinguished from each other based on the relative ratios of selected compounds [292]. Multiple regression coefficients were calculated for different samples of unevaporated and evaporated gasoline to determine, first, if the sample was a gasoline and, second, to discriminate between samples of gasoline [293]. The use of covariance mapping of GC–MS data was used to compare samples of neat ignitable liquids in the absence of background interferences [294]. Covariance mapping was used to discriminate a set of 10 unevaporated gasoline samples; however, the effects of evaporation on the mapping technique were not addressed in the article [295]. Although not intended to forensically differentiate gasoline samples, a method for obtaining the mass spectral “fingerprints” of unknown detergents in gasoline from different parts of the world has been reported [296].

Chemical fingerprinting of hydrocarbons in order to identify a spill source has received a lot of attention in the environmental forensics literature [297]. The field of environmental forensics may also prove to be a source of new techniques for forensic fire investigation. For example, some of the concepts that have been described in a four part series on the effects of refining on finished petroleum products may find an application in fire investigation [298–301]. In the area of pattern recognition analysis, extensive work has been performed on the fingerprinting of spills of heavier fuels such as jet fuel spills [302,303]. This research group has also explored the use of SPME and pattern recognition techniques to classify jet fuels by type [304]. Two-dimensional GC was used in conjunction with PCA to classify samples of jet fuel [305]. Samples of diesel fuel and jet fuel were classified using a differential mobility spectrometer (DMS) with a photoionization source interfaced to a gas chromatograph [306]. Principal component analysis was used to distinguish between samples of evaporated kerosene and diesel fuel [307]. The *n*-alkane content was used to differentiate samples of kerosene from diesel fuel [308]. An overview of the use of GC data to distinguish medium-heavy ignitable liquids found in environmental spills has been presented [309]. Mass spectra of unfragmented compounds from oil and other petroleum products, obtained using a single quadrupole LC–MS instrument, were used to chemically fingerprint different samples [310].

The use of biomarkers such as sesquiterpanes and diamondoids to characterize heavier ignitable liquids and oils has been reported and may prove to be helpful in characterizing ignitable liquids that have been solvent extracted from fire debris. A review of biomarkers, including the use of sesquiterpanes and diamondoids, to characterize oils and other petroleum products has been published [311]. Ratios of compounds from the alkylbenzene, alkylphenanthrene, and sesquiterpane classes were identified by PCA and used to differentiate samples of

diesel fuel [312]. Bicyclic sesquiterpanes were used to fingerprint diesel fuels and jet fuels and, therefore, identify the source of a spill [313,314]. The analysis for diamondoids in gasoline, and their potential use for discriminating samples, has been discussed [315].

2.9. Transfer and persistence of ignitable liquids

Information about the transfer and persistence of ignitable liquids can provide important background information for the fire investigator as well for the laboratory analyst. Passive headspace adsorption and GC–MS was used to study the persistence of solvents in floor coating materials (e.g. stain, oil finish, and polyurethane varnish) over a 2-year period [316]. The analysis of a wood deck after application of a common waterproofing material showed that a medium petroleum distillate would probably not be detected in fire debris 20–27 days after the sealer was applied [317]. A study of gasoline on interior motor vehicle carpets (floor mats) found that gasoline is unlikely to be detected after a 24 h period [318].

2.10. Contamination and background interference

Interfering compounds in fire debris samples can arise from the substrate by three different mechanisms: pyrolysis, combustion, and distillation. It is important to note that the field of fire investigation has historically used the word “pyrolysis” as a way to describe any one of these three mechanisms of generating interfering compounds. Interference products from a large number of substrates, including wood, plastics and paper products, have been reported together with the reaction mechanisms involved in the production of these compounds [319,320]. Volatile organic compounds present in a variety of unburnt substrates, as well as in the pyrolysis and combustion products from burnt substrates, have been characterized [321]. GC–MS was used to identify the pyrolysis products from different forms of polypropylene [322]. The compounds generated from the burning of television sets [323] as well as from typical (simulated) residential fires have been reported [324].

Common ignitable liquids, including Isopar H, used in the manufacture of vinyl sheet flooring have been identified [325]. The compounds that emanate from unburnt car carpets, and their interference with the identification of gasoline, have been reported [326]. The compounds obtained by partially burning some common household items, including paper products, carpet, vinyl flooring, veneer, and shoe polish have been described [327]. A commentary on this article [328] and the author’s response have also been published [329]. A study of the potential interference of a micelle encapsulator fire suppression agent on the GC analysis of fire debris samples found that, although the fire suppression agent did affect the chromatographic results, it did not interfere with the identification of common ignitable liquids [330]. A study found that some loss of volatiles from metal cans, glass canning jars, and plastic evidence bags used to package fire debris may occur when the containers are stored for 20–150 h at 66 °C, and

that an empty glass canning jar may become contaminated when stored adjacent to another jar containing volatile compounds for extended periods of time at 66 °C [331].

The collection of volatile organic compounds emanating from human skin using SPME, and subsequent analysis by GC–MS, has been reported and could provide useful background information when attempting to collect ignitable liquid residues from the skin of suspects or fire victims [332]. An open-tube pyrolysis probe was used to characterize the different type of volatiles generated by the combustion of animal and human fat [333].

3. Summary

During the review period many new books have been written for the fire scene investigator. The modeling of major fire events has been the topic of many articles with an emphasis on scene reconstruction. Little work has been published on the use of accelerant detection canines and field portable devices at fire scenes to assist the investigator in determining where a sample should be taken for laboratory analysis. The United States of America and United Kingdom are the leaders in publishing fire incident statistics. Many recent studies of fire setters and on fire setting behaviour have been published.

In the field of laboratory analysis of ignitable liquid residues solid phase microextraction has received a lot of attention but has yet to become a common technique in many forensic laboratories around the world. Separation of samples containing ignitable liquid residues was dominated by gas chromatographic methods, and the analysis of new products such as biodiesel have received some attention. The fingerprinting of gasoline and other ignitable liquids has been thoroughly studied. Little work was published on the transfer and persistence of ignitable liquid residues during this review period. Several studies have described the types of background products that may be observed in a variety of substrates, information that will assist the analyst in interpreting results obtain from fire debris samples.

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